

# Laser induced quasicrystalline order in charge stabilised colloidal systems

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We have studied the ordering of a two dimensional charge stabilised colloidal system in the presence of a stationary one dimensionally modulated laser field formed by the superposition of two modulations with wavevectors  $q_0\tau$  and  $q_0/\tau$ , where  $q_0$  is the wavevector corresponding to the first peak of the direct correlation function of the unperturbed liquid, and  $\tau$  is the *golden mean*. In the framework of the Landau-Alexander-McTague theory we find that a decagonal quasicrystalline phase is stabler than the liquid or the triangular lattice in certain regions of the phase diagram. Our study also shows a reentrant melting phenomena for larger laser field strengths. We find that the transition from the modulated liquid to the quasicrystalline phase is continuous in contrast to a first order transition from the modulated liquid to the triangular crystalline phase.

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In recent years, there has been considerable interest in the ordering of charge stabilised colloidal particles in the presence of stationary laser modulations [1–5]. Due to their large diameter and charge ( $\sim 1000e$  for a particle of diameter  $1000 \text{ \AA}$ ), charge stabilised colloidal particles have large polarisabilities. The electric field of the laser beam induces dipole moments on the colloidal particles and these dipole moments in turn interact with the laser electric field. The resulting interaction energy of a colloidal particle at position  $r$  is equivalent to an external potential  $V_e(r) = -\frac{1}{2}\chi(E(r))^2$ , where  $\chi$  is the dielectric susceptibility of the colloidal particles and  $E(r)$  is the electric field at  $r$ . This interaction causes the particles to preferentially sit at the maxima and the minima of the electric field modulations and thus promotes density modulations at twice the wave-vector of the modulating electric field. By manipulating the field pattern one can get complex structures, referred to as *Optical matter* [1], for moderate field strengths which are easily attainable in the laboratory (for recent reviews on colloids and other ref.s see [2]). When the interaction energy with the external field is of the same order as the thermal energy of the particles, ordering can take place with wavevectors other than the wavevectors of the periodic stationary external potential  $V_e(r)$ . This is due to the nonlinear coupling of the different order parameter modes. In particular, it has been observed that when the wavevector of an one dimensional laser modulation is tuned to the wavevector  $q_0$  corresponding to the first peak of the direct correlation function of the unperturbed liquid, the system freezes to a triangular lattice [3], and simulation studies [4] have also reproduced the experimental findings. Several is-

sues connected with this phenomenon of “Laser Induced Freezing (LIF)” have been explored in a recent Density functional theory [5].

Burns *et al.* [1] have demonstrated that a quasicrystalline arrangement of colloidal particles in two dimensionally confined geometry is obtainable by subjecting them to a superposition of five equiangular coherent laser beams. In their experiment the external field had the same symmetry of the final structure. A two dimensional quasicrystal is characterised by density modulations in four independent wavevectors [6]. It is interesting to ask whether one can generate LIF into a quasicrystalline structure: i.e., have the external modulation couple directly only to a few of the order parameter modes, and have the system generate density modulations with the other wavevectors needed to make up the quasicrystalline structure via the nonlinear coupling of the order parameter modes.

In this work, we show using the Landau-Alexander-McTague [7] theory that this is indeed possible, using a superposition of two 1-d laser modulations with their wavevectors tuned to be  $q_0\tau$  and  $q_0/\tau$ , where  $\tau(= \frac{\sqrt{5}+1}{2})$  is the *golden mean*. We show that in the presence of such an external modulations the system undergoes a transition to a *quasicrystalline structure* having decagonal symmetry for a certain range of parameters. We also observe a reentrant liquid phase (see figure 5).

The Landau-Alexander-McTague [7] theory is a mean field theory which expresses the free energy( $\mathcal{F}$ ) as a polynomial expansion in powers of the order parameters( $\rho_i$ ) of the system; where  $\rho_i$  are the fourier components of the density, (or better, of the molecular field) :

$$\mathcal{F} = \left[ \sum_i B_i \rho_i^2 \right] - C \left[ \sum_{i,j,k} \rho_i \rho_j \rho_k \delta_{G_i+G_j+G_k,0} \right] + D \left[ \sum_i \rho_i^2 \right]^2 + E \left[ \sum_i \rho_i^4 \right] - \sum_i V_e(G_i) \rho_i; \quad (1)$$

Here all the parameters  $B_i, C, D$  and  $E$  are assumed to be positive, and  $V_e(G_i)$  are fourier coefficients of the external modulation. To find the most stable configuration of the system for a given set of parameter values, one minimises this free energy for different choices of the order parameter sets corresponding to different lattice arrangements. The quadratic term in the free energy favours the liquid phase and the quartic terms ensure global stability. When  $B_i$  are sufficiently small, the cubic term clearly drives the system towards structures in which several sets of three wavevectors obey a triangular relationship among themselves. In the absence of external modulations, i.e., of  $V_e(G_i)$ , in 2-d this would favour

a triangular lattice. A decagonal quasicrystal would not be a stable phase, because no triangular relationships exist among the wavevectors corresponding to a decagonal symmetry.

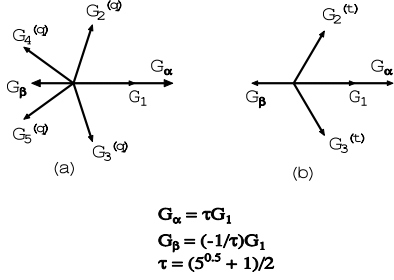


FIG. 1. Density wave-vectors corresponding to (a) modulated quasicrystal and (b) modulated triangular lattice. Note that for each density fluctuation at wavevector  $\mathbf{G}$ , density fluctuation at  $-\mathbf{G}$  also is present, though not shown in the figure.

Now consider what happens when an 1-d quasiperiodic external laser modulation potential of strength  $V_e$  at wave vectors  $\pm G_\alpha$  and  $\pm G_\beta$ , where  $G_\alpha = \tau G_1$  and  $G_\beta = -\frac{G_1}{\tau}$ , and  $G_1$  is any wavevector with magnitude  $q_0$ , is applied. Our choice of wavevectors is motivated from the fact that these wavevectors have triangular relationships with several wavevectors  $G_i$  of magnitude  $q_0$  and corresponding to a decagonal symmetry [Figure 1.(a)]. Noting that  $\tau - \frac{1}{\tau} = 1$ , we get the following three triangular relations among the wave vectors defining a decagonal quasicrystal.

$$\begin{aligned}
 G_1^{(q)} - G_\alpha - G_\beta &= 0 \\
 G_2^{(q)} + G_3^{(q)} - G_\alpha &= 0 \\
 G_4^{(q)} + G_5^{(q)} - G_\beta &= 0
 \end{aligned} \quad (2)$$

By contrast, for a triangular lattice one finds two such sets of wave-vectors which add to zero [figure 1.(b)] in the presence of the same external field:

$$G_1^{(t)} - G_\alpha - G_\beta = 0; \quad G_1^{(t)} - G_2^{(t)} - G_3^{(t)} = 0 \quad (3)$$

Note that all of the triangular relations for the decagonal quasicrystal necessarily involve the wavevectors of the external modulation potential. In contrast, only one of the two relations for the triangular lattice involves the modulation wavevectors.

Using the above relations, we can write down the free energy for a decagonal quasicrystal in the presence of our modulating potential as:

$$\begin{aligned}
 \mathcal{F}^{(q)} = & -2V_e[\rho_\alpha^{(q)} + \rho_\beta^{(q)}] + \\
 & 2B_0[\rho_1^{(q)^2} + 2(\rho_2^{(q)^2} + \rho_4^{(q)^2})] + 2B_1(\rho_\alpha^{(q)^2} + \rho_\beta^{(q)^2}) - \\
 & 2C[\rho_1^{(q)} \rho_\alpha^{(q)} \rho_\beta^{(q)} + \rho_2^{(q)^2} \rho_\alpha^{(q)} + \rho_4^{(q)^2} \rho_\beta^{(q)}] +
 \end{aligned}$$

$$\begin{aligned}
 & 4D[\rho_1^{(q)^2} + 2(\rho_2^{(q)^2} + \rho_4^{(q)^2}) + \rho_\alpha^{(q)^2} + \rho_\beta^{(q)^2}]^2 + \\
 & 2E[\rho_1^{(q)^4} + 2(\rho_2^{(q)^4} + \rho_4^{(q)^4}) + \rho_\alpha^{(q)^4} + \rho_\beta^{(q)^4}] \quad (4)
 \end{aligned}$$

Here, using symmetry considerations we have set  $\rho_2^{(q)} = \rho_3^{(q)}$  and  $\rho_4^{(q)} = \rho_5^{(q)}$ . Thus we now have five independent order parameters for the modulated decagonal structure. Accordingly we get five coupled polynomial equations from minimising the free energy with respect to these order parameters. These we have solved numerically using Newton's method of finding roots, for varying values of the parameters  $B_0$  and  $V_e$  and fixed values,  $B_1 = 0.15$ ,  $C = 1.0$ ,  $D = 0.125$  and  $E = 0.75$ , for the remaining parameters. The fixed parameter values chosen here are the same as in [3]; except for  $B_1$ , which we have chosen for convenience to be the same at  $G_\alpha$  and  $G_\beta$ , and to be much larger than the maximum value considered for  $B_0$ . This is motivated from the fact that the liquid structure factor peaks at  $q_0$  and having a density modulation at some other wave-vector will cost more energy. The qualitative features of our results are not sensitive to these specific values.

A similar, but separate, calculation is done for the triangular lattice with two independent order parameters corresponding to triangular symmetry, (since, by symmetry considerations,  $\rho_2^{(t)} = \rho_3^{(t)}$ ) and the remaining two order parameters corresponding to the external modulating field. The corresponding free energy is given by:

$$\begin{aligned}
 \mathcal{F}^{(t)} = & -2V_e[\rho_\alpha^{(t)} + \rho_\beta^{(t)}] + 2B_0[\rho_1^{(t)^2} + 2\rho_2^{(t)^2}] + \\
 & 2B_1[\rho_\alpha^{(t)^2} + \rho_\beta^{(t)^2}] - 2C[\rho_1^{(t)} \rho_2^{(t)^2} + \rho_1^{(t)} \rho_\alpha^{(t)} \rho_\beta^{(t)}] + \\
 & 4D[\rho_\alpha^{(t)^2} + \rho_\beta^{(t)^2} + \rho_1^{(t)^2} + 2\rho_2^{(t)^2}]^2 + \\
 & 2E[\rho_\alpha^{(t)^4} + \rho_\beta^{(t)^4} + \rho_1^{(t)^4} + 2\rho_2^{(t)^4}] \quad (5)
 \end{aligned}$$

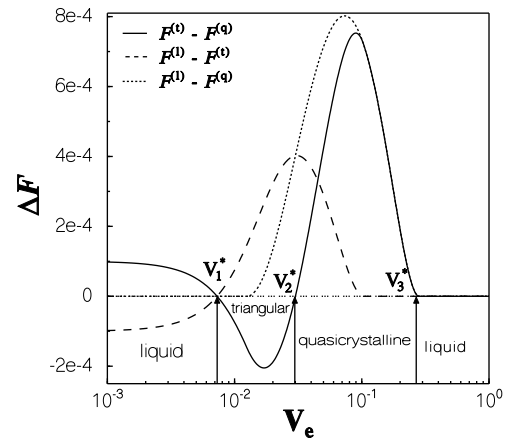


FIG. 2. Free energy difference for  $B_0 = 0.02$ . The free energy which is lower than others corresponds to the stable phase at a particular external field.

In Newton's method for root finding, when multiple solutions, corresponding to multiple minima (more gen-

erally extrema) of the free energy, are present, the solution to which the result converges depends on the initial inputs for the order parameters. In our calculations each of the two free energy functions corresponding to the triangular lattice and the quasicrystalline structure was effectively minimised with the initial guess value for the induced order parameters being 0.0 or 0.5. We found that the results converged to one of the two solutions: one corresponding to the modulated liquid phase, where only  $\rho_\alpha (= \rho_\beta)$  and  $\rho_1$  are nonzero, and the other to the modulated crystalline or the quasicrystalline phase, where the other order parameters are also nonzero. Typically, a maximum 20000 iterations were carried out in Newton's method for finding roots. It was checked that the results were not dependent on the initial guess values except for the flow to one of the two solutions alluded to above. For each parameter set the phase corresponding to the lowest free energy amongst the different solutions was chosen as the stable phase.

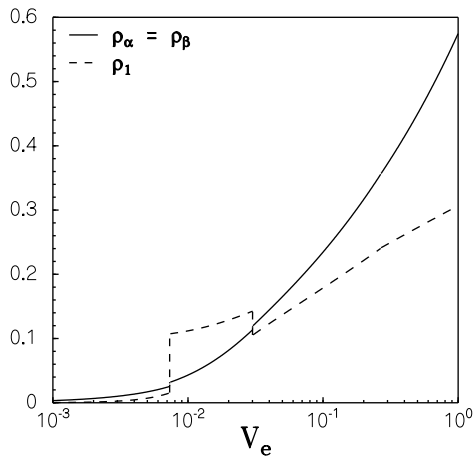


FIG. 3. Results for the order parameters ( $\rho_\alpha = \rho_\beta$ ), directly coupling to the external field and for the order parameter  $\rho_1$  with wavevector  $G_1$  parallel to the wavevector of the external modulation for  $B_0 = 0.02$ .

In Figure 2 we present results for the free energy differences for the three different kinds of order as a function of  $V_e$  for  $B_0 = 0.02$ . From these the phase with the lowest free energy is easily chosen, and the corresponding order parameters are shown in figures 3 and 4 as functions of  $V_e$ .

The full phase diagram is shown in figure 5. We term the phases as modulated, since the order parameters with wavevectors along the wavevectors of the external modulation are typically higher than those with wavevectors in the other directions.

Depending upon the value of  $B_0$ , as the external field is increased from zero, several interesting transitions are discernible from the phase diagram. For low values of  $B_0$  and of the modulation potential, the system is a triangular lattice. As the field strength is increased, the system undergoes a first order phase transition to the modulated

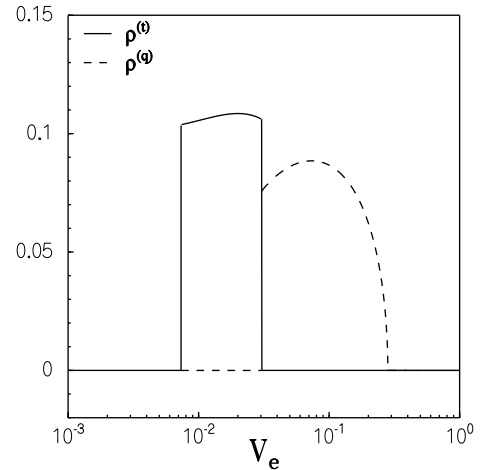


FIG. 4. Order parameters corresponding to triangular order ( $\rho^{(t)} = \rho_2^{(t)} = \rho_3^{(t)}$ ) and those corresponding to quasicrystalline order ( $\rho^{(q)} = \rho_2^{(q)} = \rho_3^{(q)} = \rho_4^{(q)} = \rho_5^{(q)}$ ) for  $B_0 = 0.02$ .

decagonal quasicrystal. At still higher field values it goes to the modulated liquid phase via a continuous transition [10].

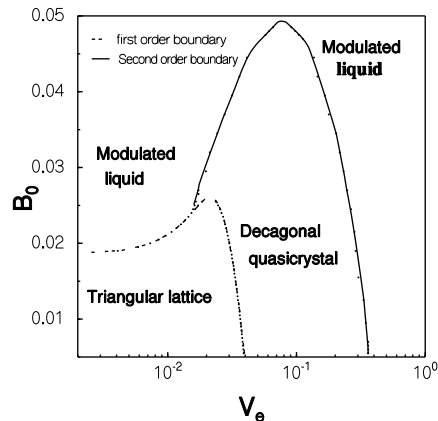


FIG. 5. Phase diagram from the Landau - Alexander - McTague theory

For  $B_0$  between 0.02 and 0.025, with increasing field strength one encounters a first order LIF transition from the modulated liquid to the triangular crystal; a first order transition from the triangular crystal to the decagonal quasicrystal and finally a continuous transition to the modulated liquid reentrant phase from the quasicrystalline phase (fig. 4).

It is worth pointing out that near  $B_0 = 0.025$  one can go from the modulated liquid directly to the quasicrystalline phase via a continuous LIF transition and thence to the triangular phase via a first order transition. With increasing field the system goes once again to the quasicrystalline phase through a reentrant first order transition. At still higher fields the transition to a reentrant

liquid phase occurs via a second order phase boundary.

For  $B_0 > 0.0265$  the system goes into the quasicrystalline order from the liquid phase via a continuous transition as the field strength is increased and then again melts to the modulated liquid phase at still higher field. Above  $B_0 = 0.05$  the system remains in the modulated liquid phase for all field strengths.

The fact that at low external fields, the system either freezes to a triangular lattice or remains a liquid depending upon the value of  $B_0$  and that the transition is first order is consistent with our knowledge about colloidal systems in the absence of any external field modulation.

At moderate field strengths, the system gains energetically by having density modulations corresponding to the wave-vectors of the modulating laser field. At higher field strengths, even though the external field modulation is 1-dimensional, density modulations corresponding to a 2-dimensional triangular or decagonal symmetry develop because of the nonlinear coupling among the order parameter modes.

At still higher fields the continuous melting is consistent with previous simulations [4] and the Landau-Alexander-McTague meanfield analysis of the laser induced freezing [3,10].

The boundary between the triangular lattice and the quasicrystalline phase is first order because the two structures are of completely different symmetry and one can not deform a triangular lattice continuously to get a decagonal symmetry.

In contrast, the phase boundary between the modulated liquid and the crystalline and quasicrystalline phases can be first order or continuous. The mechanism that determines which has been discussed in detail in ref [5]. Basically, in the modulated liquid phase  $\rho_\alpha = \rho_\beta$  and  $\rho_1$  are nonzero. Now consider setting up a Landau expansion for the free energy in powers only of the additional order parameters that characterise the crystalline or quasicrystalline phases ( i.e., with respect to the modulated liquid phase). Such an expansion has only even order invariants in the additional order parameters for the cases we are discussing. The order of the transition depends on the signs of  $T_2$  and  $T_4$ , the second order and fourth order coefficients respectively, in such an expansion. A first order transition ensues when  $T_4 < 0$ ; whereas a continuous transition results when  $T_4 > 0$ , the phase boundary being determined by the condition  $T_2 = 0$ .

When the field strength is very large, the linear term coupling the laser modulation potential with the order parameters at the modulation wavevectors seems to be the most dominant term for lowering the free energy. And we find that having density modulations along other wavevectors no longer lowers the free energy. So the decagonal phase melts to give the reentrant modulated liquid [10].

In conclusion we have shown that ,by subjecting a 2-dimensionally confined charge-stabilised colloidal liquid to a superposition of two 1-d laser modulations with their wavevectors tuned to be  $q_0\tau$  and  $q_0/\tau$  (where  $q_0$  is the

wavevector of first peak of the liquid structure factor), one can generate laser-induced-freezing into a decagonal quasicrystalline order. We have also shown that for larger laser field strengths, within mean field theory this transition is continuous and shows a reentrant melting back to the modulated liquid phase. It would be of interest if the experiments of ref. [3] can be extended to explore these transitions and the resulting quasicrystalline phase.

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